

Hydroliquefaction of Coal-Oil Agglomerates

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ABSTRACT

A novel coal hydroliquefaction process has been developed at PETC that employs a low-solvent-to-coal ($S/C = 0.35$) feed with a water-soluble dispersed catalyst. The effectiveness of liquefaction catalysts, iron and molybdenum, when loaded on the outside surface of coal-oil agglomerates is compared to that of aqueous impregnation. In the presence of 1 wt% iron and 5 vol% hydrogen sulfide, the iron-impregnated coal gave higher conversions than an agglomerated feed. Iron catalyst must be in intimate contact with individual coal particles for highest reactivity. Aqueous impregnation is, therefore, the best catalyst-loading method for dispersed iron. In the presence of 0.1 wt% molybdenum, higher conversions were, however, achieved with the coal-oil agglomerates than with molybdenum-impregnated coal. Oil agglomeration of feed coal eliminated the need for impregnation of molybdenum catalyst on the coal to achieve high conversions at low solvent-to-coal ratio of 0.35. In the absence of catalyst, higher conversions were also achieved with coal-oil agglomerates compared to a simple mixture of coal and oil at $S/C = 0.35$. The improved reactivity of agglomerates is thought to be due to the complete wetting of individual coal particles by binder oil, a hydrogen donor solvent, which was effected during the oil agglomeration step.

INTRODUCTION

During the development of novel approaches to direct liquefaction, organic solvent, water, and a water-soluble transition metal salt catalyst were found to be complementary aids to increase soluble yields of coal hydrogenation.¹ The dependence of tetrahydrofuran (THF) soluble yields on the organic solvent-to-coal (S/C) ratio of the feed described a plateau in the presence of equal masses of coal and water. Conversions reached a maximum with a small amount of solvent, $S/C = 0.5$, and additional organic solvent caused no change in soluble yields. The use of small concentrations of a water-soluble molybdenum salt effectively increased the plateau value of conversion and decreased the S/C ratio for the onset of the plateau compared to uncatalyzed systems.

Subsequently it was shown that in the presence of a dispersed molybdenum salt catalyst, conversions are independent of water partial pressure.² Yields of THF solubles in excess of 90 percent were achieved at S/C as low as 0.25 in the molybdenum-impregnated systems with no added water. The combination of 1 percent iron and 5 volume percent addition of hydrogen sulfide was found to be as effective as 0.1 percent molybdenum in low-solvent-to-coal ($S/C = 0.33$) systems.³

Low-solvent-to-coal liquefaction could potentially reduce the product recycle stream and increase throughput of the coal feed for a given size of equipment. Spherical agglomeration is considered for preparation of the low-solvent-to-coal feed because of ease of handling. Our previous work had, however, been involved with only iron- and molybdenum-impregnated coals.¹⁻³ Catalyst effectiveness by another loading method, deposition on the outside of the coal-oil agglomerates during agglomeration, has to be assessed. At a low solvent-to-coal ratio ($S/C = 0.35$), an effective liquefaction catalyst is required to prevent solvent starvation and high yields of undesired products, char and hydrocarbon gases.

Previous studies have indicated that the mode of catalyst addition is important in coal liquefaction.⁴⁻⁶ Both molybdenum and iron are effective during coal hydrogenation without organic solvent when loaded on the coal particles by an aqueous-impregnation procedure. The effectiveness of ferrous sulfate improved with prolonged mechanical mixing, but it was still less than when iron was aqueously impregnated onto the coal.^{4,5} However, Schlesinger et al.⁷ indicated that impregnation with molybdenum was not needed if the ammonium heptamolybdate was thoroughly mixed in the presence of a solvent ($S/C = 1.5$). The present research investigates the effects on conversions of the mode of catalyst addition and the form of the coal-oil feed in low-solvent-to-coal systems. Results are reported for uncatalyzed systems and with use of water-soluble salts of molybdenum and iron.

EXPERIMENTAL

MATERIAL

Minus-200-mesh grind of Illinois No. 6 (Burning Star mine) bituminous coal was used (dmmf analysis: 5.3% H, 75.4% C, 1.0% N, 3.4% S, 14.9% O). In the experiments with added catalysts, molybdenum or iron, the catalyst was loaded on the coal either by aqueous impregnation or by deposition on the external surface of coal-oil agglomerates.

In the aqueous impregnation procedure, the feed coal was prepared by mixing with water containing a dissolved transition metal salt, ammonium heptamolybdate or ferrous sulfate. The mixture was then dried in a vacuum oven at 110°C, and the catalyst deposited on the coal particles.

In the oil agglomeration procedure, a coal-derived binder oil was added to an agitated mixture of coal and water, and coal-oil agglomerates were formed into spherical particles of 2- to 3-mm-diameter size. In experiments with catalyst, the water contained the dissolved molybdenum or iron. The agglomerates were then drained by sieving. The catalyst was deposited on the agglomerates by evaporation of catalyst solution in a vacuum oven at 110°C. Previous work has shown that coal-oil agglomerates have negligible internal void, so any water adhering to agglomerates after draining was on their outer surface.⁸

For each method of catalyst addition, the catalyst concentration was either 0.10% molybdenum or 1.0% iron, reported as weight percent based on coal. The amount of catalyst deposited was calculated by measuring weight loss of water on drying. Hydrogen gas containing 5 volume percent of hydrogen sulfide was used in experiments with iron catalyst. The liquefaction solvent serving as the agglomeration binder oil was SRC II heavy distillate produced in Run 2406 at the Fort Lewis, Washington, pilot plant. The solvent-to-coal ratio was 0.35 for all experiments, i.e., those employing coal-oil agglomerates and those utilizing unagglomerated coal as feed.

PROCEDURE

Liquefaction experiments were carried out in a stirred one-liter batch reactor. The standard operating conditions for all experiments were either a 400°C or 427°C reaction temperature and a 60-minute reaction time at the desired temperature. Typically, the batch autoclave was charged with 144 gm of either a simple mixture of coal and organic solvent or a charge of coal-oil agglomerates, then pressurized (cold) to 1300 psig with hydrogen gas. The stirrer was operated at 1000 to 1100 rpm. It took from one to one and one-half hours to heat the reactor system electrically from ambient temperature to reaction temperature.

ANALYSIS

The gaseous products were metered and then analyzed by gas chromatography. The yield of C₁ through C₄ was determined as hydrocarbon gases. The hydrogen consumption was calculated from the difference between the initial hydrogen gas charged and the final hydrogen gas collected. The liquefaction residues were analyzed by solvent extraction for THF, benzene, and pentane insolubles. The conversions were calculated by

$$\% \text{ conversion} = \frac{\text{dmnf coal} - \text{organic insolubles}}{\text{dmnf coal}} \times 100\%$$

The conversions were corrected for the insolubles in the SRC II heavy distillate. It was arbitrarily assumed that the organic vehicle was inert in calculating conversions, since insolubles deriving from coal or solvent could not be distinguished.

RESULTS AND DISCUSSION

There was a concern that at the same concentration of catalyst, expressed as a weight percent of coal, agglomerates would show reactivity lower than that of feed coal for which the coal particles were individually impregnated with catalyst. Agglomerates are typically 2 - 3 mm in diameter, while individual coal particles have diameters on the order of 74 microns for minus-200-mesh grind. The catalyst deposited on the external surface of agglomerates will not be as highly dispersed as it is when impregnated on individual coal particles. Indeed, in systems containing 1.0 percent iron and 5 volume percent hydrogen sulfide, agglomerates showed liquefaction reactivity lower than

that of feed coal that was previously aqueously impregnated with iron catalyst (see Figure 1). At 400°C reaction temperature, the benzene-soluble yield was lowered by 9%, and the pentane-soluble yield by 25%. Catalytic activity of iron depends strongly on close contact of iron with coal.

In the presence of 0.10% molybdenum catalyst, oil agglomeration of feed coal, however, increased liquefaction yields (see Figure 2). At 400°C, agglomerated feed coal was more reactive than molybdenum-impregnated coal and increased substantially the liquefaction yields of soluble fractions. The benzene-soluble yield was improved by 12%, and pentane-soluble yield by 28%. At 427°C, the catalytic effect became prominent and masked the contributions of oil agglomeration. High conversions to THF and benzene solubles were obtained for both agglomerated and molybdenum-impregnated coal feeds. At low solvent-to-coal ratio of 0.35, oil agglomeration eliminated the need for impregnation of molybdenum catalyst into coal.

Since agglomerated feedstock with molybdenum catalyst showed an enhancement in liquefaction reactivity, experiments were performed to investigate the effect of the reactant form in uncatalyzed reactions. Figure 3 compares yields of soluble fractions for both agglomerated coal feed and a simple mixture of coal and solvent at the same composition without any catalysts. The liquefaction reactivity was improved dramatically with the oil-agglomerated coal compared to nonagglomerated feed. At 427°C, the enhancement in the liquefaction yields was 19% for all soluble fractions. However, conversions to solubility yields were significantly lower compared to the results obtained with catalyst-impregnated coal feed (see Figures 1 and 2).

Thus an increase in liquefaction reactivity was observed in non-catalyzed systems with oil-agglomerated coal. During coal-oil agglomeration, a water slurry of coal is first contacted with oil while being agitated. Through a series of transfer steps that occur between oil droplets and coal particles during agitation, coal particles become coated individually with oil. Subsequently, the coal particles coalesce and, with further time and agitation, form spherical agglomerates. The bridging oil in coal-oil agglomerates is thought to exist in a capillary state, giving the agglomerates a unique structure.⁸ The agglomerates are noteworthy for their compactness (absence of interior air space), sphericity, and strength. Each coal particle is completely wetted and in intimate contact with a binder oil, which is also a liquefaction donor solvent, within the agglomerate. During initial dissolution, donor solvent is readily available for donating and shuttling hydrogen. The enhanced hydrogen-transferring processes caused higher hydrogen consumption in agglomerated systems with or without any catalysts (Figures 4, 5, and 6), and improved the yields of solubles.

CONCLUSIONS

Molybdenum is effective during low-solvent-to-coal liquefaction when loaded on the outside surface of coal-oil agglomerates. However, iron catalyst must be in intimate contact with in-

dividual coal particles for highest reactivity. Aqueous impregnation is the best catalyst-loading method for dispersed iron. Oil agglomeration of feed coal increased liquefaction yields in systems with no catalyst. The unique structure of coal and binder oil, which is also a hydrogen donor solvent, in the agglomerated state enhances the hydrogen-transferring processes during initial dissolution.

ACKNOWLEDGMENT

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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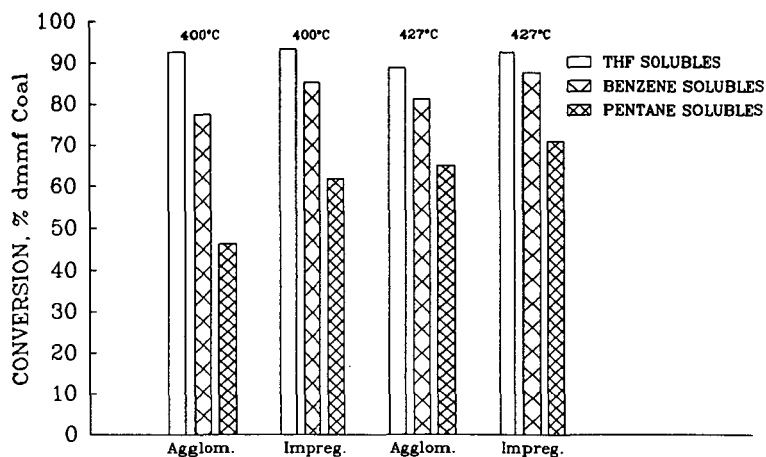


Figure 1. In Systems Containing 1.0% Iron and 5.0 Volume % Hydrogen Sulfide, Aqueous Impregnation Is a More Effective Catalyst-Loading Method than Agglomeration.

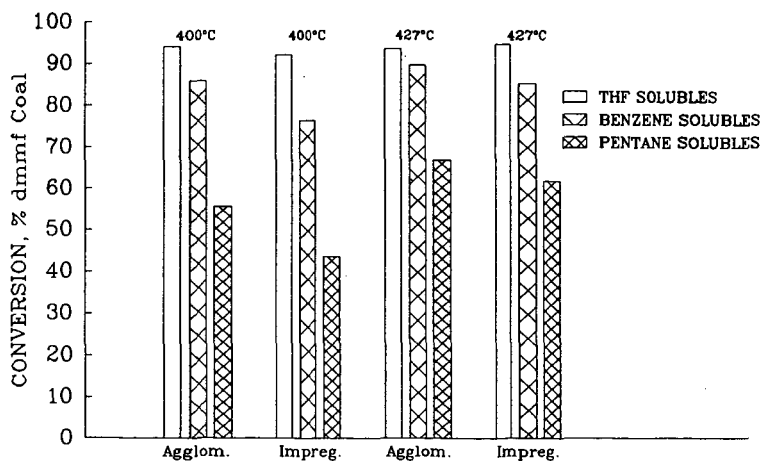


Figure 2. In Systems Containing 0.10% Molybdenum, Oil Agglomeration Improves Liquefaction Yields.

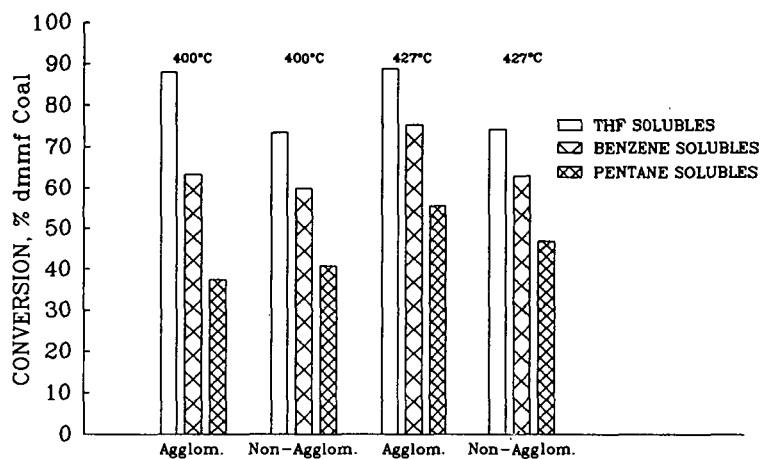


Figure 3. In Non-Catalyzed Systems, Oil Agglomeration Enhances Liquefaction Reactivity.

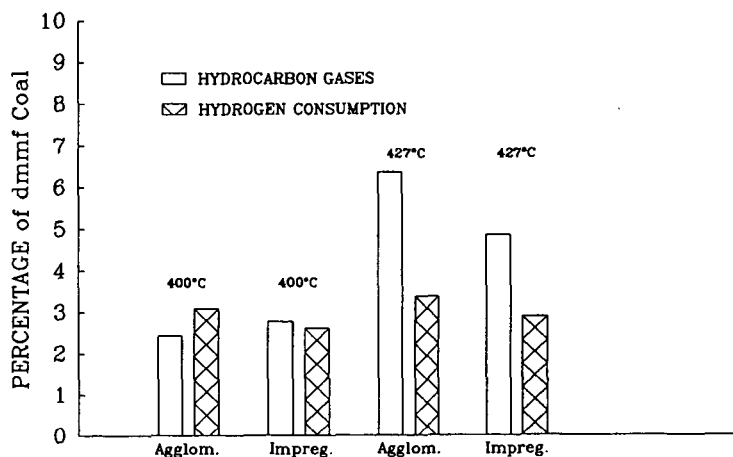


Figure 4. In Systems Containing 1.0% Iron and 5.0 Volume % Hydrogen Sulfide, Agglomerated Feed Consumes More Hydrogen.

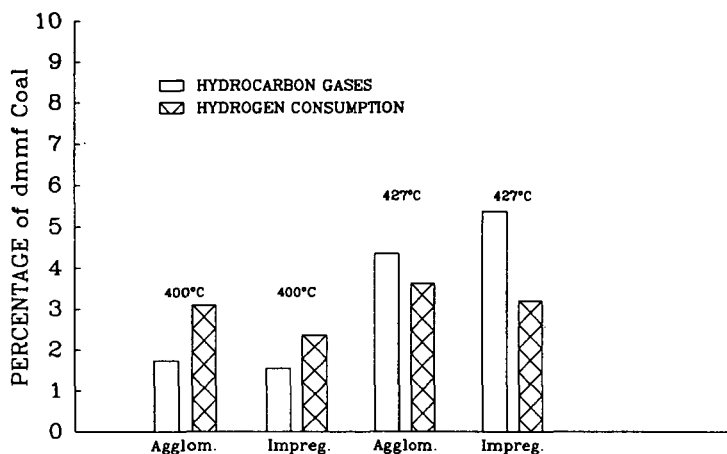


Figure 5. In Systems Containing 0.10% Molybdenum, Agglomerated Feed Consumes More Hydrogen and Produces Less Hydrocarbon Gases.

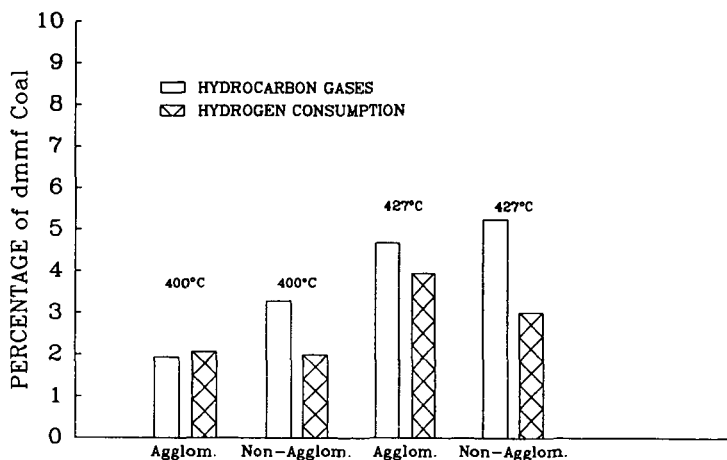


Figure 6. In Non-Catalyzed Systems, Agglomerated Feed Also Consumes More Hydrogen and Produces Less Hydrocarbon Gases.